

PATENT APPLICATION

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Title: Ultraviolet Method of Embedding Structures in Photocerams

SPECIFICATION

Field of the Invention

The invention relates to the field of microfabrication of glass ceramics. More particularly, the present invention relates to the manufacture of structure within photoactivable glasses and ceramics.

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Background of the Invention

The miniaturization processes of analytical microsystem instruments for chemical and biological assay are well known. For many microsystem applications, glass is the preferred material over metal, silicon, and some plastics, because of its transparency and inertness to biological contamination and to many caustic chemicals. However a preferred material, silicate glass, is not used often because of the difficulty of microfabricating embedded fluid channels and the difficulty of sealing open trench surface channels. Typically, fabrication of a channel or a tunnel requires cutting a trench out of a workpiece and sealing this trench with another piece of glass that is aligned and bonded on top of the open trench. A processing step could be eliminated and system reliability improved if tunnels and other three dimensional cavities could be embedded within a monolithic piece of glass. It is desirable to reliably form three dimensional embedded glass structures using suitable batch fabrication processing.

Microelectromechanical Systems (MEMS) typically disadvantageously uses two dimensional processing steps to form three dimensional structures in bulk materials. Much of the two dimensional processing is based on silicon processing steps. However, semiconductors are not always optimal materials for use in some MEMS applications. One alternative class of materials is photostructurable glass ceramics, also known as photocerams. These photostructurable materials are typically exposed by using

1 ultraviolet lamps and patterns are created using shadowmasks. The
2 glass is exposed to a critical dose and the exposed material can
3 subsequently be converted to a crystalline phase during a heating
4 step. Prior processes utilize lamps that have a spectral emission
5 that overlaps the absorption region or absorption band of the
6 photostructurable material. In this absorption region, the
7 workpiece responds to light exposure in a way that the critical
8 dose is constant and the product of irradiance and exposure time.
9 This would be considered a linear exposure process.

10 Photostructurable glass ceramics are a promising class of materials
11 for MEMS devices. Previous micromachining work with these
12 materials used conventional two dimensional photolithography
13 equipment and masking techniques. Microdrilling techniques have
14 been tried for both regular glass and photoceramic glass without
15 much success. Standard two dimensional photolithographic
16 techniques can only form planar two dimensional structures used in
17 MEMS fabrication processing to describe extruded shapes, features
18 formed by projecting a two dimensional pattern on a two dimensional
19 surface of a workpiece. Current processes can not be used to
20 create potentially useful three dimensional photoceramic structures
21 such as a simple buried tunnel in a monolithic material.
22 Furthermore, photolithographic processing of a monolithic material
23 is not amenable to undercutting of patterned structures in a way
24 that leaves anchored or suspended structures.

25
26 One prior method selectively patterns a Foturan material
27 workpiece. Foturan is a lithium aluminosilicate glass with trace
28 amounts of silver, cerium and antimony. Foturan is a trademark of

Schott Glass. The Foturan material is a photostructurable glass ceramic available in wafer form. Standard Foturan processing involves exposure of an ultraviolet (UV) lamp through a prepatterned shadowmask. Foturan has a strong spectral absorption band beginning at wavelengths lesser than 350nm. Hence, lamps with a spectral emission characteristic of 270nm to 330nm are used to expose the Foturan material because the emission band of the lamps falls within the strong absorption band of the Foturan material. Regions of the Foturan that accumulate a sufficient dose of UV light can then be converted to a crystalline material by heating the sample and etching the exposed material. Increasing the dose is achieved by increasing the intensity of the UV lamp across the spectral emission band of the lamp and or by increasing the irradiation time. The trade between intensity and irradiation time to achieve a critical dose is inverse and first order. The cerium dopant is believed to be a photosensitizer. In the presence of ultraviolet light, Ce^{3+} loses an electron to become Ce^{4+} . A fraction of the free electrons reduce trapped Ag^+ atoms to Ag^0 . In a subsequent thermal processing during heating, silver atoms diffuse together to form clusters. If a cluster is larger than 80Å, the cluster can provide the nucleus for the growth of crystalline phase material into an amorphous phase material. The crystalline phase material is composed largely of lithium metasilicate that is preferentially soluble in hydrofluoric (HF) acid. Soaking the sample in an HF solution results in dissolution of the exposed regions leaving unexposed patterned structures. The crystallized material is highly soluble in the HF acid so that soaking the patterned and heated workpiece in HF causes the

1 converted regions to dissolve away leaving the unexposed glass.
2 However, the UV exposure is commonly directed to fabricating
3 structures showing surface relief and is unsuitable for dissolving
4 the crystalline material embedded within the workpiece. Three
5 dimensional structure fabrication in photocerams can be achieved
6 using the standard method with a lamp. However, embedded structures
7 are difficult to obtain because lamp spectra is too broad and weak
8 for effective exposure within the workpiece. The photons in part of
9 the UV spectral region of the lamp are readily absorbed in the
10 material and this inundates the volume above the desired embedded
11 volume during patterning formation. The strong absorption results
12 in the conversion of all regions above the embedded volume to the
13 soluble phase. Attempts to use an unfiltered lamp would convert
14 the embedded trench structure to a trench structure open to the
15 surface. Focusing the lamp with broad spectrum light is also
16 unsuitable for forming a stacked embedded structure because regions
17 above and below the volume at the depth of focus may also
18 accumulate a dose, and over subsequent exposure operations would
19 convert to the crystalline phase preventing the formation of
20 precise three dimensional embedded structures. These and other
21 disadvantages are solved or reduced using the invention.

Summary of the Invention

An object of the invention is to provide a method for forming an embedded structure in a photoceramic material.

Another object of the invention is to provide a method for forming an embedded structure in a photoceramic material using focused pulsed laser ultraviolet light exposure.

Yet another object of the invention is to provide a method for forming an embedded structure in a photoceramic material using focused pulsed laser ultraviolet light exposure while the material is moved relative to the light source.

Still a further object of the invention is to provide a method for forming an embedded structure in a photoceramic material exposed to focused pulsed laser ultraviolet light having a spectra outside the absorption band of the photoceramic material.

The invention is a method for fabricating embedded structures in glass and ceramic materials that are photostructurable glass ceramic material, commonly called pyrocerams or photocerams. The photostructurable Foturan material is one preferred photoceram material, but many other glass ceramic materials are also suitable for photostructuring of embedded structures. The predetermined laser energy dose and wavelength settings are preferably applied to the Foturan pyroceram material, but the method can be generally applied to the whole class of photosensitive glasses. For the

1 Foturan material, the laser used is a focused pulsed ultraviolet
2 (UV) laser. The laser provides a pulsed laser beam using a lens
3 defining a beam waist at a focal depth that is moved during
4 exposure relative to the exposed material. The choice of the UV
5 wavelength is critical to be effective. The wavelength is
6 preferably at the very edge of the spectral region where photoceram
7 transitions from being strongly absorbing to weakly absorbing. In
8 the weakly absorbing spectral region, the wavelength of the laser
9 is outside the strong absorption band of the photoceram material.
10 Hence, the absorption of radiation is very small so that the
11 process is photon inefficient but enables the controlled focused
12 exposure of any volume including an embedded focal volume defining
13 an embedded three dimensional structure. The focused beam
14 illuminates the material with the intensity peaking in the focal
15 volume. The number of pulses and pulse fluence controls the amount
16 of the exposure dose so that the exposure outside the focal depth,
17 that is, outside the depth of the optical field in a collateral
18 volume is insufficient for conversion of the material to the
19 soluble crystalline phase. Within the depth of focus region, that
20 is, the focal volume, the combined effect of the focused laser beam
21 fluence ($\text{Joules}/\text{cm}^2$) and the dose in terms of the number of laser
22 pulses is beyond a critical dose that is required for conversion to
23 the crystalline phase. The focused pulsed ultraviolet laser and a
24 computer controlled sample positioning stage and shutter provides
25 motion controls for moving the material relative to the focus laser
26 beam during selective exposure of the focal volume. True three
27 dimensional patterns can be formed by moving the sample using an
28 XYZ positioning stage in XYZ directions. Motion and shutter

1 operations are both computer controlled. For example, laterally
2 moving the workpiece in the XY plane can create a tunnel, while
3 moving vertically adding via openings to the end sections of a
4 tunnel undercuts the structure above leaving an anchored but
5 suspended structure. The result is an embedded microstructure or an
6 exposed pixel defined in the focal volume.

7
8 The method can be used to create one or more stacked embedded
9 structures. There is no critical exposure above and below depth of
10 focus. The material is only critically exposed in the focal volume
11 region where the administered laser dose is above a critical dose
12 value D_c . Repeated exposures at different depth of focus enables the
13 formation of stacked embedded structures. Precise structural
14 definition is realized to create one or more embedded structures
15 because collateral volume regions above and below the focal volume
16 at the depth of focus do not accumulate a critical exposure dose.
17 The critical dose is based on sufficient per pulse fluence that is
18 the energy per unit area in a single pulse and the number of
19 pulses. For a given laser pulse width and wavelength, the per pulse
20 fluence is proportional to irradiance. The exposure process is a
21 nonlinear optical process, that is, the critical dose D_c is a
22 nonlinear function of the per-pulse laser fluence. That is, the
23 critical dose required for conversion to the crystalline phase is
24 both a function of the per pulse fluence and the number of applied
25 pulses. The dose dependence is nonlinear in per pulse fluence and
26 is cumulative. The most intense portion of the focused pulsed laser
27 light is sufficient to deliver the critical dose over a
28 predetermined number of pulses. Exploiting the nonlinear aspect of

1 the exposure process allows for creation of stacked structures at
2 any desired focal depth. The wavelength is in the weak absorption
3 region so that a critical dose is not delivered to the collateral
4 volume where the pulsed laser light is not focused and not as
5 intense as in laser focal volume where the laser light provides a
6 critical dose. Hence, the pulsed laser light has a wavelength in
7 the weak absorption region of the photoceram so that the pulsed
8 laser light passes through the collateral volume without delivering
9 a critical dose and without producing crystallization outside the
10 focal depth. The pulsed laser light is focused and intensely
11 converges for accumulation of the critical dose only in the focal
12 volume for selective critical dose exposure at the focal depth in
13 the photoceram enabling precise embedded volumetric critical dose
14 exposure. Exposing the photoceram material with higher fluence
15 focused light provides a sharp selective contrast between the
16 collateral volume and the focal volume. During fabrication, the
17 method provides a trade off between laser fluence and the number of
18 applied pulses. The critical dose of pulsed UV light provides the
19 embedded growth of an etchable crystalline phase of the photoceram.
20 By exposing bulk photoceram material to a fluence gradient for a
21 variety of pulse train lengths, and by measuring the dimensions of
22 the etched region, the proper critical dose can be determined in
23 terms of wavelength, intensity and the number of pulses.

24
25 A crystallization boundary is created in the photostructurable
26 glass where the critical dose is and is not exceeded. Above the
27 critical dose D_c , the photostructurable glass is crystallized for
28 forming a latent image in the focal volume. Below the critical dose

1 D_c , no image is formed and hence no crystallization occurs in that
2 region of the photostructurable glass. The crystallization boundary
3 separates the collateral volume from the focal volume. The
4 crystallized glass that was subjected to a dose higher than D_c in
5 the focal volume is etched away from the collateral volume of
6 photostructurable material. The under exposed uncrystallized
7 photostructurable glass in the collateral volume that did not have
8 a critical exposure remains after etching. The critical dose D_c is
9 required to create a density of nuclei large enough to result in an
10 interconnected network of crystallites. The crystallites are etched
11 away in a subsequent etching process. The density of nucleation
12 sites is proportional to the dose and the critical dose will be a
13 function of the material composition and process parameters. The
14 critical density of sites should be fluence dependent, such that,
15 $\rho = KF^m N$ Where ρ is the density of nuclei, F is the per-pulse fluence,
16 m is the power dependence, N is the number of pulses, and K is a
17 proportionality constant. A dose, D is equal to ρ/K so that $D = F^m N$.
18 For a given number of pulses, the critical dose D_c will correspond
19 to a critical fluence F_c , that is, $D_c = F_c^m N$. When a focal volume of
20 embedded photoceram material is exposed above the critical dose,
21 the focal volume can then be developed, etched, and vacated, the
22 vacant cavity defining the embedded structure.

23
24 The method enables the formation of embedded microstructures,
25 microcavities in a particular class of glass and ceramic materials.
26 The method also enables the patterned undercutting of unexposed
27 structures resulting in the fabrication of suspended or supported
28 glass and ceramic microstructures. A micromachining station

1 includes a pulsed laser that provides a focused laser beam and the
2 workpiece including the photoceram material. The laser can be moved
3 relative to a stationary workpiece, or equivalently, the workpiece
4 can be moved relative to the laser beam, both according to a
5 predefined computer program. The exposure process is maskless and
6 amenable to rapid batch fabrication of the embedded structures
7 because the only serial aspect of the process is the exposure step.
8 A parallel batch fabrication process can be used in the actual
9 material removal step. Depth control of the laser light is
10 achieved by the proper choice of exposure wavelength and focusing
11 optics. As the laser wavelength is tuned into the weak absorption
12 end of the UV absorption band of the photoceram material, the
13 absorption of laser light decreases in the collateral volume and
14 the penetration depth increases into the focal volume for
15 crystallization of embedded structures. The pulsed laser UV light
16 beam can be shaped resulting in structures that will retain the
17 beam shape. For example, a collimated beam can result in a
18 cylindrical hole. A focused beam can result in either a cone
19 section, or a hyperboloid structure.

1 The method is a direct write three dimensional volumetric
2 lithography method for selective removal of the embedded photoceram
3 material. The method is photon efficient in the sense that the
4 laser must only provide the energy to form a latent image. It does
5 not need to provide the energy to break atomic bonds and remove
6 unwanted material from the workpiece. Direct write tools, such as
7 computer aided manufacturing programs and fixtures coupled to a
8 pulsed UV laser are used in a micromachining station for rapid
9 batch processing and enhanced depth control. The pattern exposure
10 and dissolving steps can be done across an entire wafer for batch
11 processing. These and other advantages will become more apparent
12 from the following detailed description of the preferred
13 embodiment.

Brief Description of the Drawings

Figure 1 depicts embedded processing steps in apparatus form.

Figure 2 is an exposure critical fluence graph.

Figure 3 is a Foturan photoceram absorption spectrum graph.

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Detailed Description of the Preferred Embodiment

An embodiment of the invention is described with reference to the figures using reference designations as shown in the figures. Referring to the Figures, a photoceram material sample 10 is moved using a stepper motor 11 relative to a pulsed ultraviolet (UV) laser 12 radiating pulsed laser light 13 through a microscope object lens 14 providing refracted light 15 that is focused into a focused beam 16 having a focal region 18 within the sample 10. Alternatively, the photoceram material sample 10 can remain fixed and the focused laser beam 16 can be made to move. The outcome is the same. The sample material is preferably Foturan, but other photostructurable photocerams may be used. The focal region 18 has a beam waist that partially defines a focal depth into the sample 10. The sample 10 is shown having a exposed focal volumetric region 20 through which the focal region 18 had been previously stepped. The volumetric region 20 defines a focal volume of the material that has received a critical dose of illumination of the pulse laser light. The sample 10 comprising the exposed volumetric region 20 is then heated using a heater 22 and a programmed heating and cooling protocol. A hydrofluoric (HF) acid source 24 delivers a HF acid solution through an acid conduit 26. The HF acid source 24 can transport the acid to the conduit 26 either via agitation of the surrounding liquid or by high pressure focussed jets. The sample may be processed to have a top via 28 above the focal volume 30 and a bottom via 32 below the focal volume 30. The vias 28 and 32 could be formed by drilling or micromachining. The laser 12 could also be used to form the top via 28 and bottom via 32 as well as the focal

1 volume 30 using the laser exposure technique. The focal volume
2 region 20 defines the embedded structure 30. The HF acid
3 preferentially dissolves that heated crystalline material within
4 focal volume. The dissolved heat processed crystalline material is
5 flushed out of the focal volume 20 from the embedded structure 30
6 through a bottom via 32.

7
8 The laser beam 13 has a Gaussian spatial profile and a
9 predetermined number of pulses to deliver a critical dose to the
10 sample 10. The illumination source 12 may be a diode pumped Nd:YAG
11 laser that can be frequency tripled to 355nm. The pulse length may
12 be for example 8ns in duration. The beam passed through the quartz
13 object lens 14 providing an exemplar 17mm focal length. Processing
14 of the photoceram material sample 10 results in a sharp
15 differentiation between crystalline focal volumes 20 and the
16 remaining glassy collateral volumes. As the focusing beam 15
17 converges and diverges it generates a fluence gradient that
18 increases and decreases vertically through the Z direction through
19 the sample 10. Where the beam intensity exceeds the critical
20 fluence at the boundary of the focal volume 20, crystallization is
21 sharply defined. The laser fluence is at a peak intensity at the
22 beam waist 18 defined to be the focal point depth along the
23 propagation Z axis. Along the vertical Z axis, the fluence reaches
24 a maximum in the focal volume where a critical dose is delivered
25 after an accumulation of a sufficient number of laser pulses. The
26 spot size of the laser beam 16 at the beam waist 18 can be measured
27 using the knife edge method that measures power in the beam as a
28 function of the distance that a blade encroaches into the beam. By

1 fitting knife edge method data to a Gaussian profile, the spot size
2 can be determined using $P/P_0 = [\text{erfc}^{\sqrt{(2x)/\omega_0}}]/2$, where P is the optical
3 power on the detector, P_0 is the unimpeded power on the detector, x
4 is the position of the knife's edge, and ω_0 is the Gaussian spot
5 size. The material may be exposed with a wide range of spot sizes
6 including an exemplar $1/e^2$ spot radius of 0.35 mm. With a Gaussian
7 fluence profile for a predetermined spot size at a predetermined
8 wavelength, the per pulse fluence at the etch boundary and the
9 number of pulses can be determined from a log-log plot of the
10 exposure critical fluence.

11
12 Referring to all of the figures, and more particularly to
13 Figure 2, the log-log plot of the exposure critical fluence F_c can
14 be used to determine the critical dose at the etch boundary. At the
15 desired wavelength and at a desired spot size, the exposure
16 critical fluence plot can be used to determine the number of pulses
17 at a respective fluence level necessary to provide the critical
18 dose. The exposure critical fluence plot for an exemplar 355nm
19 wavelength is shown. When plotted on the log-log graph, the slope
20 corresponds to the negative reciprocal of m , the order of the
21 fluence dependence. The parameters for the log-log plot for Foturan
22 are $m=2$ and $D_c=9 \times 10^{-6} \text{ J}^2/\text{mm}^4$. D_c is a function of many parameters
23 including the laser pulse duration. The per pulse fluence
24 dependence is a squared term at the selected wavelength. The $m=2$
25 nonlinearity of the fluence indicates that the photoceram material
26 can be exposed by a low intensity lamp at the exemplar wavelength
27 but it may take an unreasonable amount of time. In the case of
28 unfocused light and with F_0 being a peak fluence incident upon the

1 sample, light is attenuated according to Beer's Law and the fluence
2 in the volume to be etched is $F_c = F_0 \exp(-\alpha z_c)$ where α is the
3 absorption coefficient and z_c is the etchable depth so that $z_c = -$
4 $[\ln(F_0^m N) - \ln(D_c)] / \alpha m$. The critical dose is a nonlinear function of
5 fluence. The slope of the log-log plot is linear within a range of
6 a suitable number of pulses, for example, between 100 and 10000
7 pulses, where $m=2$. However, outside of this number of pulses
8 range, the slope of the log-log plot may or may not abruptly change
9 when using an extreme number of fewer or more pulses for shorter
10 and longer pulse trains. It is desirable to operate with a
11 wavelength where the photostructurable glass-ceramic responds to
12 light with a nonlinear dependance on per pulse fluence and where
13 the photostructurable glass-ceramic is weakly absorbing. At
14 wavelengths where the material has significant absorption, the
15 absorption coefficient can increase with increasing dose. For
16 example, for a small number of pulses of 266nm light, the material
17 might have an absorption coefficient of 3.4 per millimeter and for
18 a large number of pulses, the absorption coefficient might be 5.4
19 per millimeter. Within an acceptable range of pulses, the log-log
20 plot has a linear slope for determining a critical dose that is
21 highly predictable. The number of pulses can be delivered in a
22 pulse train as a pulsed illumination sequence for pixelized pattern
23 exposure of the sample 10.

24
25 The photoceram material can be developed using a programmable
26 furnace or heater 22. The temperature can be increased at 5°C/min
27 to 500°C and held for an hour. At this temperature, the latent
28 image is developed by diffusion of neutral silver atoms that form

1 silver clusters in the critically exposed focal volume. The
2 temperature is raised again preferably to 605°C at 3°C/min and held
3 for another hour. At this higher temperature, a crystalline phase
4 is nucleated from the vitreous phase at the silver clusters. The
5 crystalline phase, also known as the ceramic phase, is slightly
6 less dense than the amorphous phase, so there is a small expansion
7 associated with the devitrified regions. The temperature is
8 sufficient for softening of the amorphous phase so the glass flows
9 slightly to accommodate the expanded volume. After completing the
10 nucleation and growth steps, a Foturan sample has an image
11 consisting of brown crystalline focal volumes 20 in a clear
12 amorphous matrix of the collateral volume.

13
14 In the crystalline phase, the sample material is more rapidly
15 soluble in hydrofluoric acid 24 than the surrounding material in
16 the collateral volume. In a 5% solution of hydrofluoric acid 24 at
17 room temperature, the etch ratio is about 50:1. With an exposure
18 using a 355nm Gaussian beam, the dark focal volume region 20 is
19 crystalline and colored by silver clusters after an appropriate
20 thermal treatment. Where the material 10 did not exceed the
21 critical dose, the crystallite density is insufficient to form an
22 etchable volume. When the material is exposed by a focused
23 Gaussian beam, the dose will be maximized at the center of the
24 focal region. The dose is reduced in every direction from that
25 point. Where the dose drops to less than the critical dose, the
26 crystallite density will be too sparse to allow further etching.
27 This etch boundary sharply defines the embedded cavity. The
28 embedded cavity 30 may be few microns in diameter with a smooth or

1 rough texture. After the sample is exposed and heated, the sample
2 is then etched. The size of the etched focal volume can then be
3 determined by optical microscopy to confirm that the wavelength and
4 number of pulses are suitable for providing the critical dose at
5 the focal depth.

6
7 The focal volume is preferably defined using computer aided
8 manufacturing. The laser can be step moved relative to a sample of
9 photoceram or alternatively the sample can be step moved relative
10 to the laser. In the case of step moving the laser, at each step,
11 the laser delivers a pulsed illumination sequence comprising a
12 pulse train of a predetermined number of pulses that critically
13 expose the photoceram at the focal depth in a small pixelized
14 volume. The laser is then repeatedly step moved, and another pulse
15 train of exposure is delivered at each step, so that a large focal
16 volume is created comprising a plurality of the pixel volumes. In
17 this manner, computer controlled steps are used to form any size
18 embedded volume 30 as well as top and bottom vias 28 and 32.
19 Computer controls are well suited for fabricating stacked embedded
20 structure across an entire wafer for cost effective batch
21 processing.

22
23 The method is directed to exposing photoceram material by a
24 focused pulsed UV laser having a wavelength in the weak absorption
25 region but with the laser light focused to expose the material with
26 a critical dose in a focal volume using a predetermined number of
27 focused laser pulses that forms an embedded latent image which, can
28 be transformed into an embedded crystalline region following a

1 proper heat treatment. The method can be used for forming embedded
2 tubes, tunnels, cone, hyberboloids, and other shapes with a single
3 exposure inside a monolithic glass sample. The fabrication of
4 embedded three dimensional microstructures in glass and ceramic
5 materials may be critical to the future development of photonics
6 and communication systems, display screens, nanosatellites,
7 microthrusters, microlamps, biocompatible chemical instruments,
8 microoptics, and microfluidics. Many of these applications will
9 benefit from a process for embedding structures with features sizes
10 in the tens of micrometers. Those skilled in the art can make
11 enhancements, improvements, and modifications to the invention, and
12 these enhancements, improvements, and modifications may nonetheless
13 fall within the spirit and scope of the following claims.

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